

IMPROVED OXIDE CATHODE AND ITS MANUFACTURING PROCESS

The present invention relates to the field of electron tubes, and especially cathodes whose function 5 in these tubes is to emit electrons and thus constitute the source of an electron current.

More particularly, the invention relates to so-called oxide cathodes. These cathodes, which are the most widely used, comprise a layer of oxides which are 10 strong electron emitters on one face of a metal support. The support is connected to an electric potential which is negative relative to the surrounding potential, allowing an electron flux to be emitted from the oxide layer.

Figure 1 is a simplified sectional view showing 15 a cross section through a conventional oxide cathode 2. The support 1 consists of a thin nickel plate forming a pill which has a face 1a covered with an oxide layer 3 in the form of a washcoat. The washcoat is a coating 20 consisting of an active compound filler and of a binder. The active compound is generally based on barium carbonate ( $BaCO_3$ ) and on carbonates of other elements, which are subsequently converted to barium oxide ( $BaO$ ) and oxides of other elements.

25 The oxide layer normally has to be at a relatively high temperature to emit. In the conventional case of a so-called indirectly-heated cathode, a heat source, such as a filament, is provided near the support and connected to a low-voltage current source.

In operation, an electron current flows though 35 the thickness of the oxide layer 3 (arrow I) due to the effect of the surrounding electric field. The electric field is created by establishing a potential difference between the support 1 and an electrode 5 located near the external surface 3a of the layer 3. In the example, the support is referenced at an earth voltage while the electrode 5 is biased at a high positive voltage +V. The electron flux obtained by the cathode 2 is

proportional to the intensity of this electron current I..

Figure 2 shows the same cross section through the cathode 2 after it has changed over time. It may be seen that a resistive layer 6, called an interface layer, has grown between the metal support 1 and the washcoat layer 3.

In some applications, it is necessary to try to obtain as high an electron current in the cathode as possible. This is especially the case with cathode-ray tubes for "multimedia" and "high-resolution" display screens, as well as for video projectors and other types of electron tubes, such as those used in the microwave field.

It is known that the intensity of the electron current that can be obtained from an oxide cathode is limited because it does not have a high enough conductivity. This is essentially the conductivity through the thickness of the washcoat layer 3 and the interface layer 6 - that through the support 1 may be regarded as negligible. It should be noted that the conductivity of a layer is inversely proportional to its resistivity.

Moreover, it appears that oxide cathodes do not withstand a high current density well, particularly when the current is constant over time, on account of their insufficient electrical conductivity.

It is generally accepted that the insufficient electrical conductivity of oxide cathodes is due to two parameters: the fact that the emissive washcoat 3 is based on oxides which by nature are poor conductors and the fact that the resistive interface layer 6, between the metal of the support 1 and the washcoat, grows.

Figure 3 is an equivalent electrical circuit of the components R1 and R2 of the electrical resistivity of the oxide cathode, deriving from the emissive washcoat layer 3 and from the interface layer 6, respectively. As these two layers are superposed, the components R1 and R2 combine as resistors in series.

The contribution of the washcoat layer 3 to the electrical resistivity changes over the lifetime of the cathode. This is because metallic barium is created in this layer by the reaction between the barium oxides 5 BaO and the reducing elements which diffuse out of the nickel. This metallic barium, the primary role of which is to move to the surface of the washcoat in order to allow electron emission, gives the washcoat electrical conductivity. However, the amount of metallic barium 10 decreases for two reasons:

- the generation of metallic barium is gradually exhausted because of the fact that the reducing elements must come, by diffusion, from an increasing depth in the nickel; and
- 15 - the interface layer 6 itself acts as a diffusion barrier with respect to these reducing elements.

The contribution of the interface layer 6 to the electrical conductivity changes during the lifetime because this interface grows. The growth of this 20 interface is due to chemical reactions between the washcoat and the reducing elements contained in the nickel (such as Mg, Si, Al, Zr, W, etc.) which accumulate compounds in this interface. These compounds are rather poor conductors since they are, above all, 25 oxides such as MgO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Ba<sub>2</sub>SiO<sub>4</sub>, BaZrO<sub>3</sub>, Ba<sub>3</sub>WO<sub>6</sub>, etc.

The origin of the electrical resistivity of oxide cathodes and its changeover time have been studied in the prior art for the purpose of increasing 30 the electron current density that can be sustained.

Certain known solutions aim to reduce the resistivity of the oxide layer 3 by generally incorporating a conductive filler into it. For example:

- patent US-A-4,369,392 proposes to incorporate 35 nickel powder into the washcoat, which in this case is carried out by pressing and then sintering;

- patent US-A-4,797,593 provides a solution which comprises adding scandium oxide or yttrium oxide to the

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washcoat, one of the effects of which is to improve the electrical conductivity;

5 - patent US-A-5,592,043 proposes a washcoat in the form of a solid object containing metals (W, Ni, Mg, Re, Mo, Pt) and oxides (of Ba, Ca, Al, Sc, Sr, Th, La) which increase the electrical conductivity by a "percolation" effect; and

10 - patent US-A-5,925,976 proposes the addition of metals (Ti, Hf, Ni, Zr, V, Nb, Ta) to the washcoat.

Other known solutions aim to attenuate the effect of the interface layer 6. For example:

15 - patent US-A-4,273,683 pertains to the case of an interface formed above all from  $\text{Ba}_3\text{WO}_6$ . A layer of nickel powder is deposited on the nickel support prior to washcoating and, in addition, a barium carbonate concentration gradient is produced in the thickness of the washcoat. The  $\text{BaCO}_3$  concentration is less in the region touching the interface, so that less  $\text{Ba}_3\text{WO}_6$  compound is created;

20 - patent US-A-5,519,280 describes a solution in which indium tin oxide (a complex based on  $\text{In}_2\text{O}_3$  and  $\text{SnO}_2$ ) is incorporated into the washcoat and acts by providing conductivity and by limiting the growth of the interface;

25 - patent US-A-5,977,699 proposes the addition of a zirconium (Zr)-based layer between the nickel of the support and the washcoat, this layer decreasing the interface in terms of its reducing-agent property; and

30 - in the minutes of the conferences "International Vacuum Electron Sources Conferences" IVEESC98, which were held at Tsukuba (Japan) on 7-10 July 1998, the publication entitled "An analysis of the surface of the NiW layer of tungsten film coating cathode" by Takuya Ohira et al. describes a solution in which a layer of 35 tungsten powder is deposited on the nickel of the support prior to the washcoating and explains that this layer has an effect of dispersing the reducing elements (Si and Mg) so that the compounds (especially  $\text{Ba}_2\text{SiO}_4$ ) resulting from the chemical reactions at the interface

are less concentrated and that, consequently, the interface is less of a barrier.

It has also been proposed in patent US-A-4,924,137 to ensure that the barium produced by reaction between the oxide layer and the support is absorbed in the washcoat rather than disappearing by evaporation. For this purpose, scandium oxide and an oxide of Al, Si, Ta, V, Cr, Fe, Zr, Nb, Hf, Mo, or W are incorporated into the washcoat.

Finally, solutions have also been proposed in the context of so-called directly heated cathodes. By way of example, patent US-A-4,310,777 recommends, in the case of a nickel support having a large amount of tungsten, a small concentration of zirconium in the nickel within a relatively narrow range. Similarly, patent US-A-4,313,854 proposes, in the case of a nickel support with a high percentage of refractory metal, interposing a layer of metal (Si, B, Ti, Zr, Hf, V, Nb, Ta, Mo, or W) carbides between the nickel and the washcoat so as to limit in this way the growth of the interface.

It should be noted that the solutions of the prior art do not consider, in a unitary way, the properties associated on the one hand with the oxide layer and on the other hand with the interface layer.

Moreover, other types of cathodes exist, called impregnated cathodes, which allow a sustained regime with a high electron current, even if this current is constant over time. These cathodes comprise a porous metal pill impregnated with an emissive material. However, they are complex and their manufacturing costs exclude them from many applications, especially in cathode-ray tubes intended for the commercial market.

In the light of the foregoing, the subject of the present invention is an oxide cathode comprising a support and an oxide layer on the support. It furthermore includes particles of a conducting material having a first end incorporated in the support and a second end lodged in the oxide layer, so as to

constitute conducting bridges passing through an interface layer forming between the support and the oxide layer.

Advantageously, the conducting material of the 5 particles is a carbide of one or more metals, for example:

- metals of Group IVB, and preferably at least one metal from: titanium (Ti), zirconium (Zr) and hafnium (Hf);

10 - metals of Group VB, and preferably at least one metal from: vanadium (V), niobium (Nb) and tantalum (Ta);

15 - metals of Group VIB, and preferably at least one metal from: chromium (Cr), molybdenum (Mo) and tungsten (W).

The support may be made of metal, preferably a nickel-based metal.

The invention also relates to an electron tube, for example a cathode-ray tube, comprising an oxide 20 cathode of the aforementioned type. The cathode-ray tube may be intended for so-called "multimedia" television applications.

The invention also relates to a process for manufacturing an oxide cathode in which an oxide layer 25 is deposited on a support, this process comprising the steps consisting in:

- furnishing that surface of the support which is intended to receive the oxide layer with particles of conducting material so that the particles have a first 30 end incorporated in the support and a second end which is exposed; and

- covering the surface with an oxide layer.

According to a first method of manufacture, the step of furnishing the particles of conducting material 35 consists in spreading the particles out over said surface and in applying a force to the particles in order to encrust the first end of the particles in the support.

According to a second method of manufacture, the step of furnishing the particles of conducting material consists in incorporating the particles in the support and in making the second end of the particles 5 stand out by a surface treatment, for example by means of selective chemical etching treatment.

The particles may be incorporated into the support during the metallurgical production of the latter.

10 When the support is formed by drawing, the second end of the particles is exposed either before or after the drawing.

15 The invention and the advantages which accrue therefrom will be more clearly apparent on reading the description which follows preferred embodiments, given purely by way of non-limiting example, with reference to the appended drawings in which:

- Figure 1, already described, is a partial sectional and simplified view of a conventional oxide cathode and of an electrode used for creating an electric field conducive to electron emission;

- Figure 2, already described, is a partial and simplified sectional view of a conventional oxide cathode in which an interface layer has formed;

25 - Figure 3 is a theoretical electrical circuit showing the contribution of the oxide layer and of the interface layer to the electrical resistivity of the cathode of Figure 2;

30 - Figure 4 is a partial and simplified sectional view of an oxide cathode according to the present invention;

- Figure 4a is a magnification showing in detail the imbrication of a particle of conducting material in the cathode of Figure 4;

35 - Figure 5 is a theoretical electrical circuit showing the components contributing to the electrical resistivity of the cathode of Figure 4;

- Figures 6a to 6c illustrate various steps in the production of a cathode according to a first method of

manufacture in accordance with the present invention; and

5 - Figures 7a to 7d illustrate various steps in the production of a cathode according to a second method of manufacture in accordance with the present invention.

The base structure of a cathode 2 in accordance with the invention is illustrated schematically by the sectional view in Figure 4. This illustration is similar to that in Figure 2 and the common parts of 10 these two figures bear the same reference numbers.

Thus, the figure shows a nickel-based conducting support 1 on a surface 1a of which an oxide layer 3 in the form of a washcoat is deposited. In use, an interface layer 6 forms between the aforementioned 15 surface 1a and the oxide layer 3, as described previously with reference to Figure 2.

In the examples which follow the case of an indirectly heated oxide layer will be considered, that is to say a cathode which is heated to temperature by a 20 heat source external to the support 1, for example by means of a filament near the support and connected to a low-voltage current source. However, the invention may also apply in the case of a directly heated cathode.

In accordance with the invention, the cathode 2 includes particles 8 of conducting material which are 25 located at the boundary between the support 1 and the oxide layer 3. The particles 8 are distributed approximately uniformly over the entire surface (or at least part of it) occupied by the oxide layer 3.

30 As shown in greater detail in Figure 4a, each particle 8 has a first end 8a which penetrates the aforementioned surface 1a of the support 1 so as to be encrusted in the support and a second end 8b which is lodged in the thickness of the oxide layer 3. These two 35 ends 8a and 8b are, within the limit of the irregularity in the shape of the particle, mutually opposed on an axis A perpendicular to the surface 1a of the support.

An intermediate part 8c of the particle passes right through the thickness of the interface layer 6. The particle 8 therefore constitutes a conducting bridge which establishes an electrically conducting 5 link connecting the body of the support 1 to the terminal point of the second end 8b, that is to say within the oxide layer 3.

It should be noted that the mean particle size compared with the thickness of the oxide layer 3 may be 10 tailored so that the projection P along the aforementioned axis A of that part of a particle 8 which is lodged in the oxide layer 3 occupies a greater or lesser proportion of the thickness E of this layer according to the desired properties.

15 The effect of the presence of the particles 8 on the lowering of the electrical resistivity due to the oxide layer 3 and to the interface layer 6 will now be analyzed with reference to Figure 5.

In this figure, it is assumed that the cathode 20 2 is referenced at an earth potential, as in the case of Figures 1 and 3, and the electrical resistivity of the support, this being a good conductor, is neglected. We consider the electrical resistivity in the direction 25 of axis A perpendicular to the general plane of the cathode 2 over a section starting from the aforementioned surface 1a of the support and ending on the exposed surface 3a of the oxide layer. This section is divided into two parts: a first part containing the thickness of the oxide layer 3 and a second part 30 containing the thickness of the interface layer 6. Since these parts are superposed, their resistivities combine additively. The resistivity of the first part is denoted R3 (to be compared with R1 of Figure 3) and the resistivity of the second part is denoted R4 (to be 35 compared with R2 of Figure 3).

The resistivity R4 of that part of the cathode 2 which contains the interface layer 6 appears to be negligible. This is because, the particles 8 being good conductors, this layer is effectively short-circuited

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by the conducting bridge effect that each particle 8 provides. Moreover, all the particles 8 together constitute a set of parallel connections distributed over the entire active surface of the oxide layer.

5 With regard to the electrical resistivity R3 of that part of the cathode 2 which contains the oxide layer 3, this is also lower than the resistivity R1 of a conventional cathode without the particulate material. This is because the penetration of the 10 particles 8 within a certain proportion of the layer 3 also creates a conducting bridge effect within the latter. The electrical resistivity is improved in this proportion.

Thus, by providing the presence of imbricated 15 conducting particles 8 in accordance with the present invention, a reduction in the resistivity both of the interface layer 6 (this becoming virtually zero) and of the oxide layer 3 is obtained by this unique means.

Preferably, a material is chosen for the grains 20 8 which satisfies several criteria: to be hard enough to be able to be encrusted in the nickel (or other metal) of the support 1, not to poison the emission from the cathode 2, to be an electrical conductor, to withstand oxidation (especially that caused by the 25 conversion of the carbonates into oxides), to be chemically stable and especially not to react with the elements of the cathode, and not to evaporate excessively nor to diffuse excessively under the operating conditions of the cathode.

Metals having a relatively high melting point 30 oxidize more than nickel does and therefore do not represent the best solution, and metal oxides may prove not to conduct electricity sufficiently. On the other hand, optimum realization may be achieved using metal 35 carbides. Among the latter, it may be advantageous to choose one or more from:

- carbides of Group IVB, and especially of titanium (Ti), zirconium (Zr) and hafnium (Hf);

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- carbides of Group VB, and especially of vanadium (V), niobium (Nb) and tantalum (Ta); and

- carbides of Group VIB, and especially of chromium (Cr), molybdenum (Mo) and tungsten (W).

5 This is because the metal carbides listed above satisfy all the criteria:

a) they are very hard (Vickers hardness > 1000 HV);

10 b) they are chemically stable and even inert, and consequently cannot be cathode emission poisons;

c) they are good electrical conductors (electrical resistivity < 100  $\mu$ ohms.cm);

15 d) they have a very high oxidation resistance (for example, tantalum carbide (TaC), niobium carbide (NbC) and zirconium carbide (ZrC) withstand oxidation in air up to approximately 800°C); and

20 e) they evaporate very little since they are thermally very stable because of their high melting point (for example, hafnium carbide (HfC), niobium carbide (NbC), tantalum carbide (TaC), titanium carbide (TiC) and zirconium carbide (ZrC) have melting points greater than 3000°C, which are among the highest of all materials.

A first method of manufacturing oxide cathodes 25 in accordance with the invention will now be described with reference to Figures 6a to 6c.

The method begins with a cathode preform simply comprising the conducting support 1. In the example, this is a continuous strip of nickel-based material 1 30 which will be cut and drawn in order to form the support in all its final dimensions. As shown in Figure 6a, a powder composed of particles 8 of one or more metal carbides according to the composition described above is spread out over a surface 1a of this strip.

35 Next, that part 8a of the particles 8 which forms the end in contact with the surface 1a is encrusted in the material of the support 1 by applying a compressive force to the opposite end 8b of the particles in the direction of the arrow F (Figure 6b).

Several techniques may be used to apply this encrustation pressure. In the example illustrated, the latter is obtained by means of a vertical press 10 positioned above the particles and controlled in order 5 to obtain the desired degree of encrustation. It is also conceivable to pass the strip 1 with its surface deposit of powder between a pair of compressing rolls in order to obtain the same technical effect. If necessary, the support 1 may be heated in order to 10 allow better penetration of the particles 8.

Once the particles 8 have been encrusted, the oxide layer 3 is deposited so as to cover the exposed portions of the surface 1a of the strip and of the particles 8. In the example, the layer completely 15 embeds the exposed parts of the particles. The particles therefore have one end 8a incorporated in the nickel and one end 8b in the washcoat, and thus form conducting bridges as explained above.

The layer 3 is prepared in the form of a 20 washcoat consisting of one or more carbonates and a binder. Typically, as carbonates, barium, strontium and possibly calcium carbonates are used. The interface layer 6 is not illustrated in the figure as it does not appear and develops only during ageing of the cathode 25 2, by conversion of that part of the oxide layer near the surface 1a of the support. It is possible to determine the thickness of this interface layer in advance and consequently to ensure that the height of the non-encrusted parts of the particles 8 is 30 sufficiently great to pass right through this thickness and thus fulfil its function of conducting bridge.

Another method of manufacturing the cathode 2 in accordance with the present invention will now be described with reference to Figures 7a to 7d, in which 35 method the particles 8 are incorporated in the constituent material of the support 1 during the metallurgical production of the latter. In this case too, the support is a nickel-based support.

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In the example illustrated in Figure 7a, the support 1 is in the form of a metal tape during the phase of incorporating the particles 8. This tape will then be cut and drawn in order to obtain the support in 5 its final shape.

The tape 1 is moved in the direction of the arrow G by means of rollers 12 so that its surface 1a intended to receive the oxide layer runs in succession past a heat source 14 and a gun 16 which sprays the 10 particles 8. The composition of the particles used for this technique may be the same as that for the first method of manufacture.

The function of the heat source 14 is to raise the temperature at the surface 1a sufficiently for the 15 metal of the strip to be softened (plastic phase). The heat source may be a device for inducing eddy currents in the metal strip 1.

The gun 16 sprays the particles 8 forcibly against the surface 1a of the tape. Since this surface 20 has been softened, the particles penetrate entirely or almost entirely into the body of the strip and are therefore immersed in the latter, near the surface 1a, as shown in greater detail in Figure 7b.

Next, the strip 1 is subjected to a selective 25 chemical etching treatment for the purpose of removing the constituent material of this strip at its surface 1a without altering the composition of the particles. In the example, this etching treatment is carried out by depositing an acid 18 in liquid phase on the surface 30 1a of the tape (Figure 7b). Other techniques may be envisaged, such as vapour etching or plasma etching.

After the chemical etching treatment, the ends 8b of the particles 8 facing outwards stand out from the surface, while the opposite ends 8b remain 35 imbricated in or integral with the body of the constituent material of the strip 1, as shown in Figure 7c. This result is obtained because of the fact that the metal of the support 1, in this case nickel, is less resistant to the chemical etching or plasma

etching treatment than the metal carbides constituting the particles.

5 Next, as shown in Figure 7d, a washcoat layer 3 containing carbonates, and especially barium carbonate, forming the emissive part of the cathode, is deposited on the surface 1a and the projecting parts of the particles 8.

10 As in the first method of manufacture (cf. Figure 6b), the exposed parts of the particles 8 after the chemical etching treatment project sufficiently from this surface 1a to pass through any interface layer and penetrate the oxide layer of the cathode.

15 Finally, the strip thus prepared is cut into cathode support preforms and then drawn in order to obtain the body of the cathode.

20 In a variant of the process according to this second method of manufacture, the aforementioned cutting and possible drawing are carried out before the chemical etching or similar step. In other words, the end 8b of the particles 8 is exposed once the support 1 is in the preform state or in its final state.

25 Finally, another variant of the first method of manufacture consists in incorporating the particles throughout the thickness of the support 1 during one step in the production of this strip. In this case, those of the particles lying close to the surface 1a will serve as conducting bridges when their ends 8a have been embedded in the washcoat 3 and the other particles will be inactive, without disturbing the 30 operation of the cathode.

35 It will be understood that the oxide cathode according to the present invention has very wide applications, including all fields in which oxide cathodes are normally used: display tubes (CRTs), microwave tubes, grid tubes, etc.

The invention lends itself to many variants not described, which remain within the competence of those skilled in the art and within the scope of the claims,

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especially with regard to the choice of materials, the dimensional parameters and the manufacturing processes.